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# RAPID GROWTH OF POTASSIUM DIHYDROGEN PHOSPHATE CRYSTALS

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## Abstract

We report the development of a process for high rate (15 mm/d) growth of potassium dihydrogen phosphate single crystals. Correlations for mass transport by convective diffusion (to cones or disks under axially-impinging flow) are applied to published rate data on 3-mm KDP crystals to derive a semi-empirical kinetic equation for (101) growth rate measured in the z direction:

$$g_z = k_g \exp(-H_g/RT)(c_s - c_{sat})^n,$$

where the coefficients found by linear regression are  $k_g = 3492$  m/s,  $H_g = 41399$  J/mol and  $n = 2.277$ ; and  $c_s$  and  $c_{sat}$  are, respectively, the surface- and saturation concentrations [kg-KDP/kg-water]. Material properties, transport, and kinetic equations are then solved numerically to predict the dependence of growth rate on temperature, supersaturation, and the ratio of flow rate to a crystal dimension. The model is experimentally verified for 20-25 mm crystals grown at rates of 5-25 mm/d using a turbine to enhance solute flux to the pyramidal faces. We conclude that high growth rate of large crystals is possible and scales according to the ratio of characteristic velocity to crystal dimension.

## Introduction

The research described in this report has the objective of increasing the rate of growth of potassium dihydrogen phosphate (KDP) single crystals from the current industrial rate of 1.5 mm/d to about 15 mm/d. The higher rate would reduce the time for boule growth from a year to a month. This would effect a roughly proportionate decrease in production cost of what is now a highly capital intensive process. In addition, we have the broader objective of establishing a scientific and engineering basis for the development of economical processes for growth of any optical crystal from solutions or fluxes under analogous conditions of mixed kinetic and mass-transport control.

Researchers have long recognized the influence of solution convection on crystal growth rate and perfection. (See Laudise<sup>1</sup> for general discussion.) The problem of mass transport becomes acute with KDP boules grown for laser fusion applications because of the large dimensions (0.3 m x 0.3 m x 0.5 m) and the objective of high growth rates. Moreover, high growth rates are generally accompanied by uncontrolled growth of the prismatic (100) faces. This generally induces habit modification, inclusions and internal stresses, and coloration. These effects are related to the tendency of the (100) faces toward incorporation with high segregation coefficients of cation impurities.<sup>2,3,4</sup>

Classical crystal growers make use of numerous natural or forced solution convection schemes. Belyustin and Stepanova<sup>5</sup> perfected a static cell capable of sustaining natural convection currents between a saturation chamber and an underlying growth chamber held at a slightly lower temperature. More commonly, a mild forced convection is used to promote stable and unflawed growth at reasonable rates (up to a few mm/d for KDP). In the Holden cell,<sup>6</sup> crystals revolve at the ends of horizontal beams attached to a vertical drive shaft.<sup>7,8,9</sup> If baffles are placed about the walls of the tank, high relative velocities can be achieved with continuous rotation at the expense of increased turbulence and danger of spontaneous precipitation or flawed growth.

Batyreva et al.<sup>10</sup> used boule rotation about the z axis to provide a uniform flow with a minimum of turbulence in a system capable of producing crystals of dimensions 0.16 m x 0.16 m x 0.35 m. Rotation of the boule in this manner causes the (101) faces to act as a weak centrifugal pump. At each point on the pyramid, there is a net component of solution velocity which is normal to and impinging upon the growth surfaces. This provides a roughly uniform flux of solute to the growth surfaces at a rate proportional to the square root of rotational rate.

Yokotani et al.<sup>11</sup> used an impeller placed directly above a boule oriented with the z-axis vertical. However, the solution flow direction was from the bottom of the tank, upwards along the prismatic faces, and thence toward the apex of the pyramid. This configuration does not provide a flow which impinges on the growing (101) faces, thus defeating the salient advantage of forced convection.

Parvov<sup>12,13</sup> used a centrifugal impeller provided with a housing and nozzle to convert the centrifugal movement of the solution into a jet directed downwards onto a stationary crystal. The pump was used in a three-chambered growth system to produce ammonium dihydrogen phosphate boules with 50-mm cross-sectional dimension.<sup>14</sup> While this technique should be capable of sustaining a stronger impinging flow and higher growth rates than achievable with boule rotation alone, there was no indication that this was the objective.

Very high rates of growth of 30-40 mm wide crystals have been reported by Besspalov et al.,<sup>15</sup> although no information was given concerning flow or cell configuration other than to claim that the method was capable of "growing crystals in the form of single-sector blocks at a rate of 0.5-1 mm/h with a specified orientation of the z-axis and the desired shape of the cross section."

The barrier to high rate KDP growth is clearly not associated with surface kinetics. One of us (Cooper) has measured z-direction rates of perfectly formed microscopic crystals to 100 mm/d. Mullin et al. (16) has grown 3-5 mm crystals in a tubular flow channel to rates of 40 mm/d.

There appear to be three barriers to achieving high rates with use of current industrial processes: (1) Bulk transport of dissolved KDP from the supply vessel into the growth chamber is insufficient to support high growth rates.<sup>17</sup> (2) Transport of the solute across the diffusion boundary layer adjacent to the growing crystal is hindered. (3) The industry does not directly measure or control supersaturation which is related to the driving force for crystal growth. As part of our project, Zundeleovich investigated the first area, and conducted a heat and mass transport analysis of a canonical growth system with separate chambers for crystal growth, stock dissolution, and superheating in order to determine transfer rates required for high-rate growth of large crystals.<sup>17</sup> This study did not identify a practical cell configuration for overcoming the mass transport limitation at the crystal/solution interface. Therefore, we developed the semi-empirical model reported here (based on hydrodynamics, mass transport, and growth kinetics) and used it to predict the operating conditions required to grow large crystals at rates up to 1 mm/h in three different growth cell configurations. The model has been verified for 20-25 mm crystals grown at rates to 1 mm/h using a turbine to enhance solute flux to the pyramidal faces. Finally, we discuss three in situ, non-destructive techniques for continuous measurement of supersaturation through differential measurements of solution density, buoyancy, and electrical conductivity.

#### Growth of Crystals at High Rates under Mixed Kinetic and Mass Transport Control

Derivation of a Kinetic Equation for Crystal Growth. The growth of crystals from multicomponent solutions or fluxes will in general be jointly controlled by surface-kinetic and bulk-diffusion processes. Crystal growth kinetics will generally depend on the solute activity at the crystal/solution interface through its effect on the rate of progression (and in some cases, nucleation) of microsteps. However, the crystal will grow at the rate at which new material is brought to the interface by diffusion. Diffusion can be enhanced considerably with

forced convection of the solution. A steady state growth process may occur when the rate of diffusion is just matched by the rate of incorporation of the solute into the crystal lattice. In this case, a time-independent concentration profile is established for which the limiting gradient at the crystal/solution interface is related to the flux through Fick's law. In the simplified picture of Figure 1, the rate of crystal growth is determined by the equilibration of the interfacial rate (dependent on the supersaturation level,  $c_s - c_{sat}$ ) with the diffusion rate, which is controlled by the excess of bulk concentration over the surface concentration ( $c_b - c_s$ ) and by the width of a diffusion boundary layer. The width of diffusion boundary layer in turn is a function of system geometry, solution flow conditions, and physical properties of the solution.

We derived a kinetic equation for KDP crystal growth at high rates from published rate data on 3-mm KDP crystals grown under impinging solution flow using the cell depicted in Figure 2.<sup>16</sup> In this work, growth rate in the z- (i.e. [001]) direction was reported as a function of flow rate, temperature, and bulk concentration. To describe the growth of the pyramidal (101) surfaces, we assumed an empirical kinetic equation of the form;

$$g_z = k_g \{ \exp(-H_g/RT) \} (c_s - c_{sat})^n \quad (1)$$

where R is the universal gas constant, T is absolute temperature, and n,  $H_g$ , and  $k_g$  will be treated as adjustable parameters. (Here and throughout this communication, concentration is given in mass-ratio units, kg-solute/kg-solvent.) From geometrical considerations, the required flux to the (101) surfaces depends on z-direction growth rate and crystal density,  $d_{KDP}$ , according to:

$$j = g_z d_{KDP} \sqrt{2}/2 \quad (2)$$

The mass-transport rate to the pyramidal faces was approximated by correlations for cones under axially-impinging flow.<sup>18,19</sup> We chose the characteristic dimension X to be the height slant of the pyramid, in lieu of the generatrix of the cone. The transport correlations, plotted in dimensionless form in Figure 3, may be expanded to the following equation for flux, j:

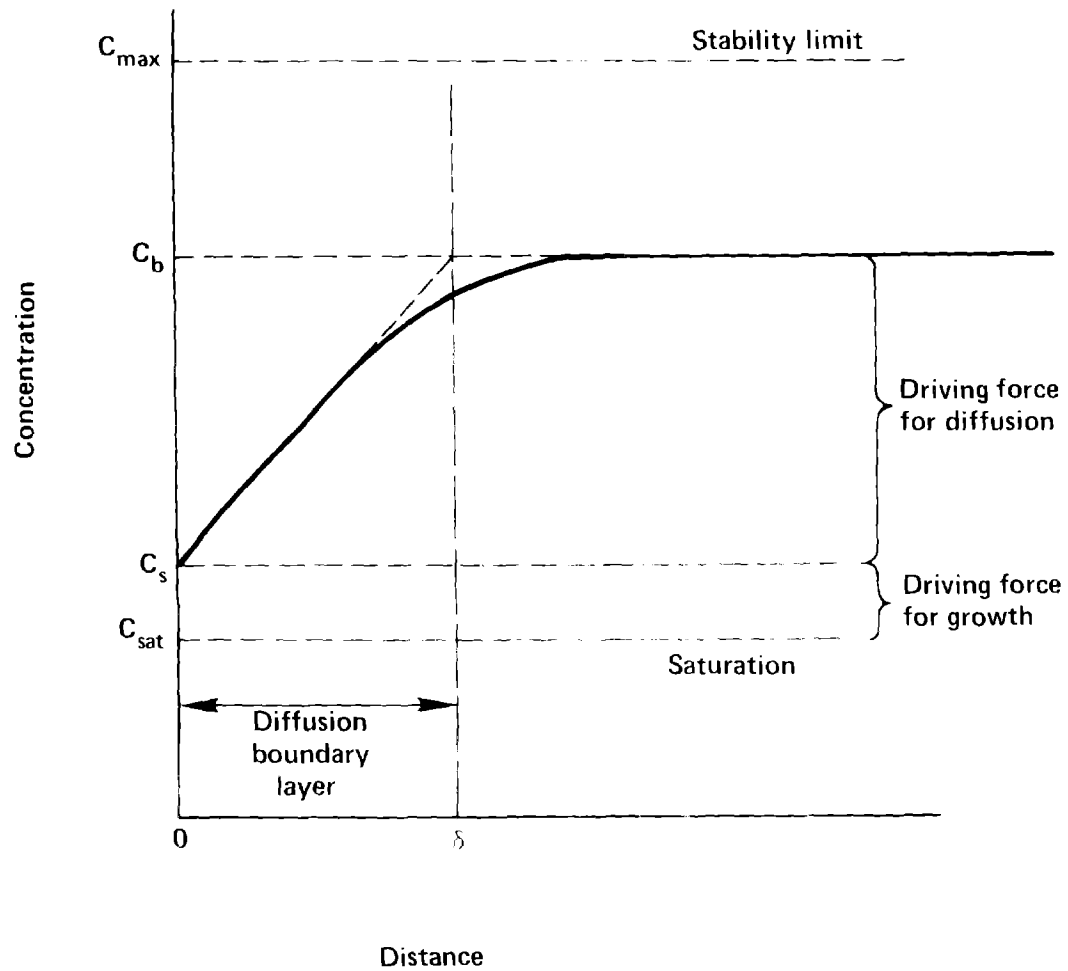


Figure 1. Concentration profile in the solution adjacent to growing crystal, with reference to solubility ( $C_{\text{sat}}$ ).



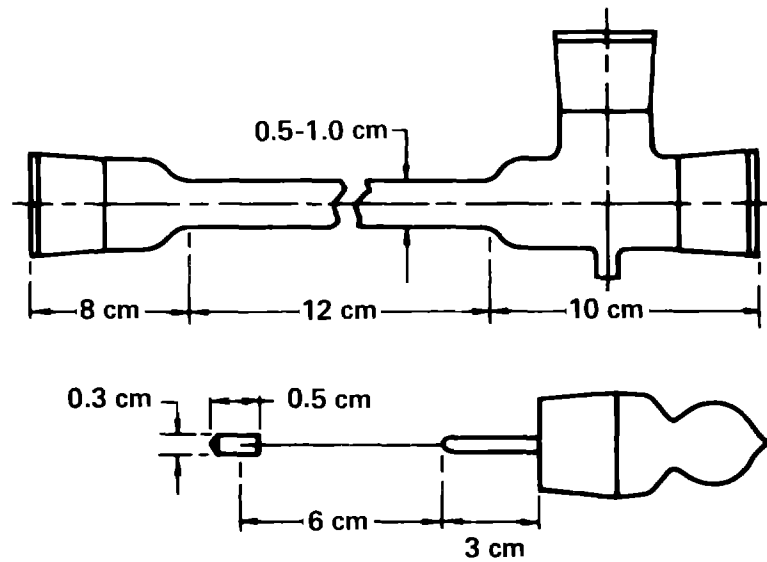


Figure 2. The tubular flow channel used by Mullin and Amatavivadhana<sup>16</sup> in studies of growth of small KDP crystals under impinging flow.

$$j = 0.8 D \left\{ d_b \frac{c_b}{1+c_b} - d_s \frac{c_s}{1+c_s} \right\} \left( \frac{U}{Xv} \right)^{1/2} \left( \frac{v}{D} \right)^{1/3} \quad (3)$$

where  $D$  is diffusion coefficient,  $d_b$  and  $d_s$  are solution density in the bulk and at the surface, respectively,  $U$  is potential flow velocity (taken as the axial velocity in flow tube), and  $v$  is kinematic viscosity. From equation (3) it is seen that transport depends on the ratio,  $U/X$ . Using the published data base of growth rate, bulk concentration, together with the diffusion coefficient and viscosity data given in the same paper,<sup>16</sup> equations (2,3) were solved for  $c_s$ .<sup>20</sup> Finally, we derived estimates of  $k_g$ ,  $H_g$ , and  $n$  from the data for  $g_z$ ,  $c_s$ , and  $T$  by regression of a linearized form of equation (1). The estimates are:

$$\begin{aligned} k_g &= 3492 \text{ m/s} \\ H_g &= 41.399 \text{ kJ/mol} \\ n &= 2.277 \end{aligned} \quad (4)$$

Equation (1) is plotted in Figure 4, together with the computed values of surface supersaturation. The data fits the correlation with a standard deviation of 5%.

**Materials Properties Correlations.** We determined the solubility and density of KDP solutions over a wider range than reported in ref. 16 and reduced the data by linear regression to equations of the form:

$$c_{\text{sat}} = k_0 + k_1 t + k_2 t^2 \quad (5)$$

$$d = d_0 + d_1 c + d_2 c^2 + d_3 t + d_4 t^2 \quad (6)$$

Data for kinematic viscosity and diffusion coefficient reported by Mullin were similarly reduced:

$$v = v_0 + v_1 c + v_2 c^2 + v_3 t + v_4 t^2 + v_5 ct \quad (7)$$

$$D = D_0 \exp(-D_1/RT) \quad (8)$$

In (5-7),  $t$  is temperature ( $^{\circ}\text{C}$ ). The values of the coefficients and ranges of the data bases are given in the appendix.

**Dependence of Growth Rate on Operating Conditions and Scale.** Three growth chamber configurations were chosen for analysis: (1) pyramidal growth under axial flow; (2) growth of sector disks or blocks cut from the (101) plane, with perpendicularly impinging flow; and (3) single

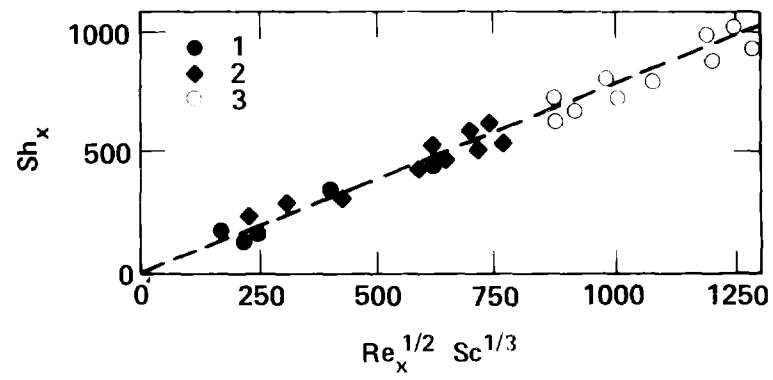


Figure 3. Transport correlations for (1) disks, (2) right-angle cones and (3) 30° cones under axially-impinging flow conditions.<sup>18,19</sup>

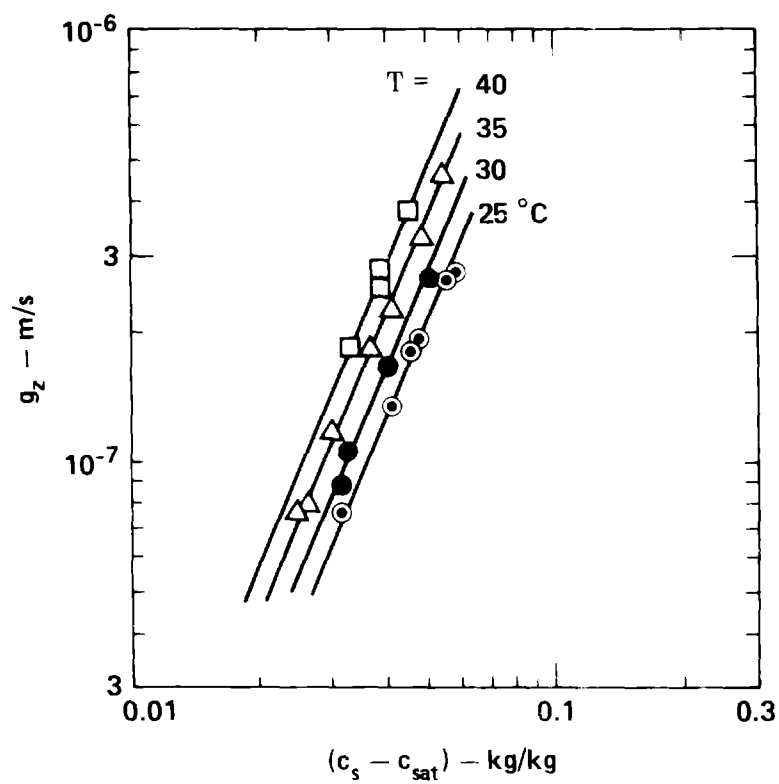


Figure 4. Growth rate of KDP from equations (1) and (4) with data derived from Mullin.<sup>16</sup>

crystal sectors positioned flush with floor of a narrow rectangular-duct flow channel, under conditions of laminar or turbulent flow. For pyramid growth, equations (1-8) were solved numerically to obtain the functional dependence,  $G$ , of growth rate on temperature, bulk supersaturation, and a hydrodynamic parameter,  $U/X$ .

$$g_z = G(T, \sigma, U/X) \quad (9)$$

Here the bulk concentration is conveniently expressed as a dimensionless supersaturation,  $\sigma$ :

$$\sigma = (c_b - c_{sat})/c_{sat} \quad (10)$$

Curves of constant growth rate are plotted on axes  $T$  and  $\sigma$  in Figure 5. The effect of the hydrodynamic parameter  $U/X$  is shown in Figure 6. Also plotted in these figures is an estimate of the upper boundary of the metastable range suggested by Loiacono.<sup>4</sup>

The results shown in Figures 5 and 6 are nearly identical with those for the sector block when the characteristic dimension is taken as the radius of the circumscribed circle. Analogous results are obtained from the analysis for the flow channel in either turbulent or laminar flow, for small ratios ( $< 0.03$ ) of the channel depth to crystal length measured in the direction of flow.

In summary, we predict growth rates of 15 mm/d or more for relative supersaturations below about 0.1 and at temperatures above about 50°C in both impinging and parallel flow systems. At higher temperatures the required supersaturation is predicted to decrease relative to the metastable limit of the solution. The process scales according to the ratio of characteristic velocity to crystal dimension. This ratio is inversely proportional to the square of diffusion boundary layer thickness. For a fixed growth rate, the process is controlled completely by kinetics in the limit as  $U/X$  approaches infinity, or by mass-transport, as  $U/X$  approaches zero. Full details of the computations including computer codes are available in reference (20).

**Experimental Study of Crystal Growth.** Crystals of 20-25 mm cross section ( $X = 14-18$  mm) were grown at rates to 25 mm/d at temperatures from 50-67°C using a novel turbine (Figure 7) to enhance mass transport.

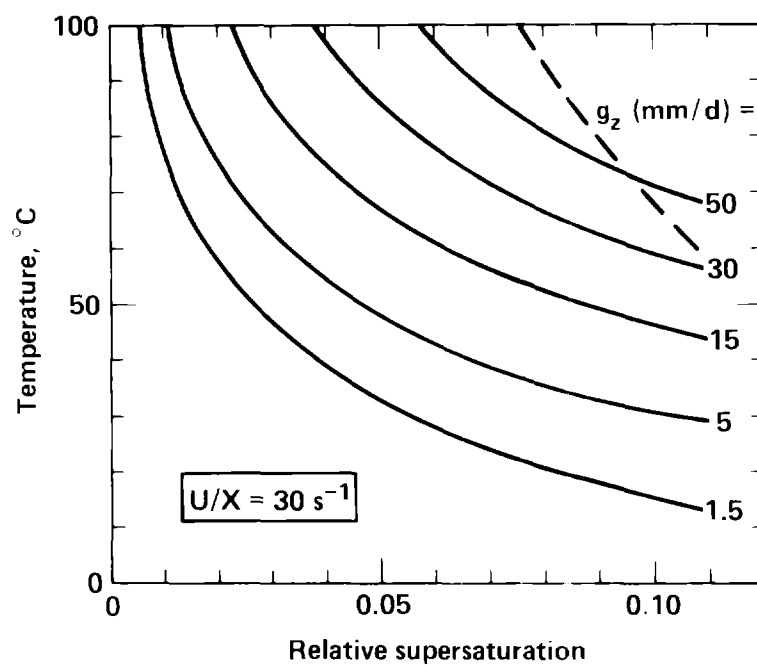


Figure 5. Curves of constant growth rate as a function of temperature and bulk relative supersaturation for a fixed hydrodynamic parameter,  $U/X$ .

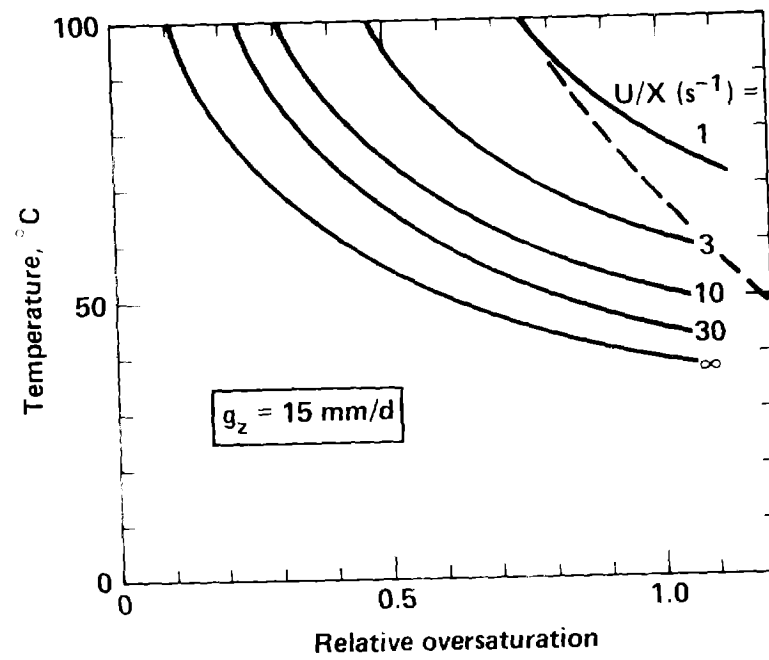


Figure 6. Curves of 15 mm/d growth rate for different degrees of kinetic control indicated by  $U/X$ .

The crystal seed was attached to the turbine such that its axis of rotation coincided with the z axis of the crystal. Flow rate was 0.3 m/s at 30 rpm.

Figure (8) shows the z-direction growth rates computed on the basis of equation (9), the integrated rate (crystal tip displacement), and the experimental displacement. The agreement is excellent, given the order of magnitude difference in scale between the data base and our experiments, the extrapolation to higher temperatures, and the approximations involved in the transport model.

Preliminary measurements of laser damage on samples grown at 5 to 25 mm/d indicate damage thresholds which are comparable to, or greater than, those of industrial crystals grown at 1-1.5 mm/d.<sup>21</sup> Breakdown occurred generally above 5 J/cm<sup>2</sup> for 1-ns pulses of 1064 nm laser light. The crystal habit was similar to that of crystals grown at lower rates, and inclusions or coloration were not evident in the (101) growth. Growth on the (100) surfaces, however, was flawed. Spiral growth hillocks were evident on the (100) surfaces, but not on the (101) surfaces.

The Determination of Supersaturation. The driving force for crystal growth is related to the difference between surface concentration and solubility. Only bulk concentration is accessible to direct measurement. Bordui and Loiacono<sup>22</sup> have developed correlations for concentration, temperature and electrical conductivity. They used absolute measurements of the latter two variables to determine concentration for control purposes. The narrowness of the metastable concentration range requires that a property such as density or conductivity be measured with extreme precision (eg., 0.1%) for both growth and saturated solutions, if supersaturation and hence growth rate are to be accurately controlled (to 10%). Such precise measurements are feasible,<sup>22</sup> but some difficulty can be avoided by measuring directly the difference between a property of the growth solution (e.g., buoyancy, refractive index, electrical conductivity or density) and that of a reference solution of known concentration (possibly saturated) contained in a separate vessel within the growth tank. We have used differential hydrometry to detect changes in concentration to levels of 0.5 g-KDP/kg-water during the growth of a crystal, while systems based on



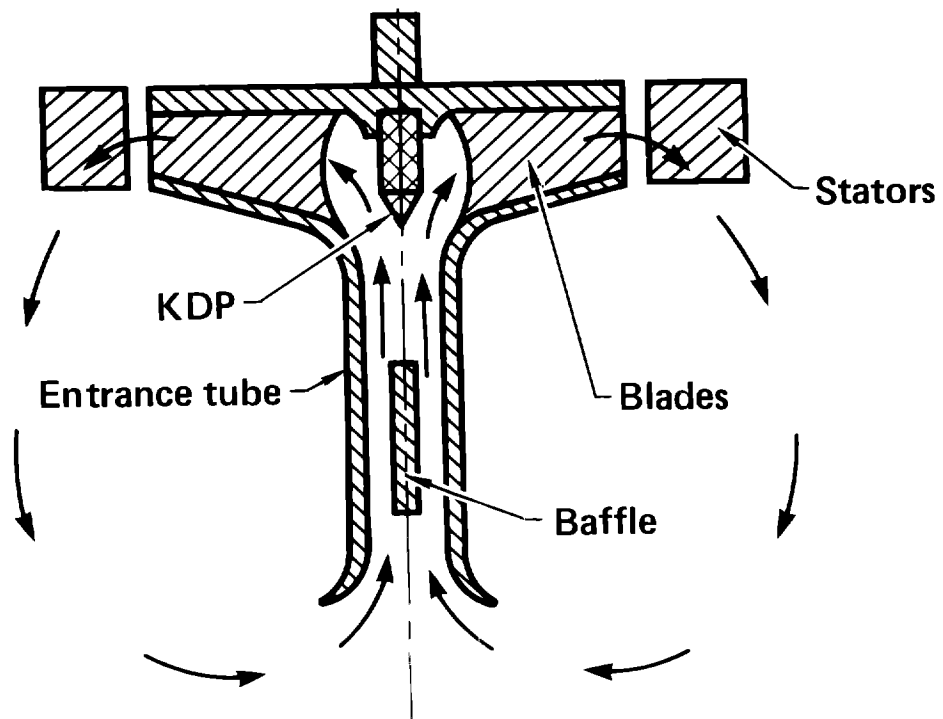
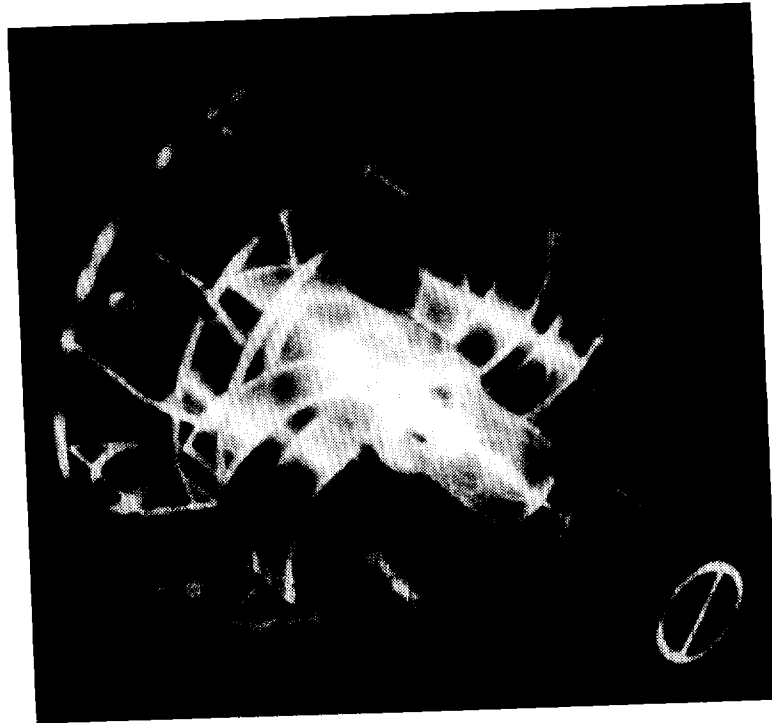


Figure 7. Turbine and peripheral stators used in studies of crystal growth at rates to 1 mm/h. The diagram shows flow configuration. Turbine diameter is 180 mm.

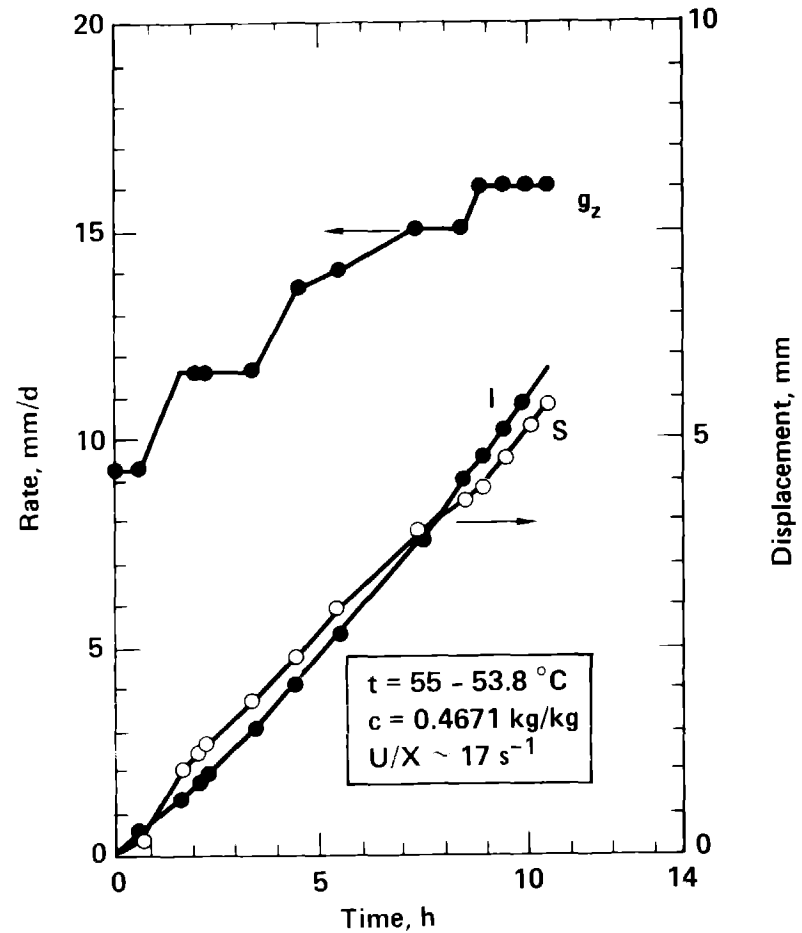
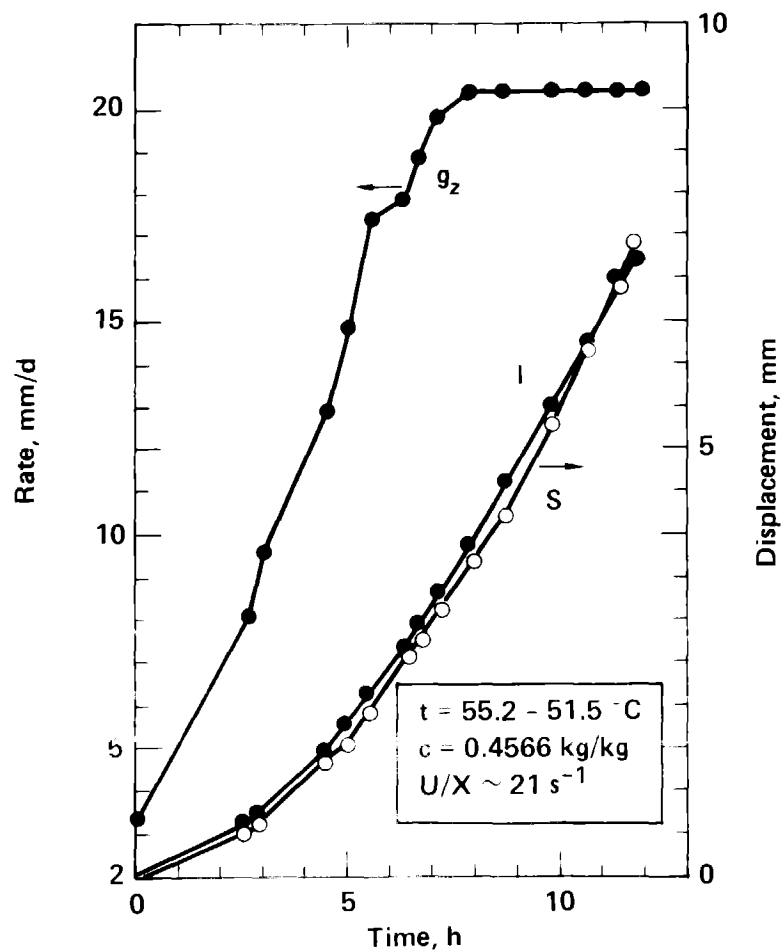


Figure 8. Comparison of ( $g_z$ ) computed growth rate, ( $I$ ) integrated growth rate or computed displacement, and ( $S$ ) experimental displacement crystal tip for typical growth experiments conducted at fixed concentration by temperature drop method; arbitrary time zeros.

differential buoyancy and electrical conductivity which are more appropriate for industrial use have been described.<sup>20</sup> For example, two electrical conductivity cells (one filled with a reference solution and the other with the growth solution) may be connected as elements of a Wheatstone bridge to generate a signal proportional to the concentration difference.

### Conclusions

High-rate growth of KDP crystals is feasible within the metastable concentration limits of the growth solution. High rates can be achieved under impinging solution flow with the use of an efficient turbine. The process scales according to the ratio of flow rate to crystal dimension, which is inversely related to diffusion boundary layer thickness. Growth in flow channels is also feasible and has the advantage of achieving the required flux in the laminar flow regime which should be more resistant to spontaneous nucleation.

The elongation growth was free of inclusions and showed laser damage thresholds at least as high as for slow-grown material. Prismatic growth was rapid and highly flawed with veil inclusions. Therefore, it will be necessary to constrain prismatic growth with the use of mechanical barriers or sheaths, as has been the practice with other crystals.<sup>13</sup>

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Appendix. Values of Regression Coefficients and Data Base Ranges for Material Properties Correlations.

Property:	$c_{\text{sat}}$ (kg/kg)	$d(\text{kg/m}^3)$	$\nu(\text{m}^2/\text{s})$	$D(\text{m}^2/\text{s})$
Equation:	(5)	(6)	(7)	(8)
Coefficient #				
0	1.9888E-1	1.01395E3	1.7419E-6	3.7670E-7
1	5.4556E-4	6.24803E2	1.7921E-6	1.5817E4
2	7.0005E-5	-2.37293E2	3.5005E-6	---
3	---	-2.50180E-1	-4.5279E-8	---
4	---	-2.71869E-3	4.8783E-10	---
5	---	---	-4.0703E-8	---
Data Base Range Temperature, °C	30-90	35-60	20-40	20-40
Reference	this work	this work	(20,16)	(20,16)